EXPLORATORY STUDY ON THE BEHAVIOUR OF GLASS/PDCPD COMPOSITES

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ABSTRACT

The potential of the tough thermoset polydicyclopentadiene (PDCPD) as a matrix for composite materials was explored in this study. A range of properties was compared for a composite with a PDCPD formulation matrix and an equivalent epoxy composite. The PDCPD composite showed higher interlaminar fracture toughness and reduced damage development during tensile loading. Improved fatigue life and higher compressive strength were observed. Impact damage was greatly reduced and substantial improvement in compression after impact strength was noted. Based on the obtained results, the PDCPD formulation used in this work can be considered an interesting alternative for brittle thermosets.

1 INTRODUCTION

Thermosets are easily available and allow for versatile and efficient composite production processes to be used, like RTM or vacuum infusion. Normal epoxies and polyesters, however, are brittle. Composites using these materials as a matrix are generally also brittle materials, and thus sensitive to impact and they often fail in an explosive manner.

Numerous attempts have been made to improve the toughness of thermosets or to find new thermosets with enhanced toughness. Toughening of epoxy resins can for example be done by adding rubber particles, thermoplastic particles or other additives [1, 2].

The effect of using tougher matrices, like toughened thermosets or thermoplastics on the mechanical properties of composites has been investigated by many researchers e.g. in [3-7]. Poon et al. [5], for example, made an assessment of the impact damage in composites produced from different types of toughened epoxies. They noted less pronounced impact damage and significantly higher compression after impact strength. Vieille et al. [6, 7] looked at the impact and post-impact properties of PPS and PEEK based laminates and observed about 50% lower delamination area after impact compared to epoxy counterparts for an impact energy of 10J. Similar results were obtained by Bishop for a carbon-PEEK laminate compared to a carbon-epoxy laminate [8]. Manjunatha et al. [9, 10] looked at the tensile fatigue behaviour of a silica nanoparticle-modified glass fibre reinforced epoxy composite. These researchers noted improvements of up to 10 times in fatigue life by the addition of silica nanoparticles. Böger observed similar results [11].

Toughening epoxies or polyesters also has drawbacks, like a substantial increase in viscosity, which encumbers the production process of composites. Some thermosets that possess inherent toughness do exist, however. A relatively young, high toughness thermoset that seems promising for use in composites is polydicyclopentadiene (PDCPD) [12]. PDCPD is obtained through ring opening metathesis polymerisation (ROMP) of DCPD monomers upon the addition of a metathesis catalyst.

Different formulations of PDCPD exist, with variations in the properties as a result. Some properties of the formulation used in this study are listed in Table 1.

Because of the very low viscosity, DCPD formulations can offer fast and efficient fibre wetting within a short time period. The tunable nature of the metathesis catalysts allows the material to be suitable for a very fast processing (fast RTM) or showing extended working lifetime at room temperature and be thermally triggered on demand. The chemical nature of PDCPD makes it resistant towards hot, wet and corrosive environments.

Very limited studies have been looking into the mechanical properties of composites with PDCPD matrix. In the framework of the SNL/MSU/DOE project on wind turbine blade materials, however, an extensive experimental program including also some tests on this type of materials has been carried out [13-15]. It should be noted that the PDCPD used in the mentioned study was a particular formulation called Proxima™ (Materia, Inc.). Not many details about this material are known, but it probably contains some modifiers to make it compatible with an existing, commercial coating or treatment. The Proxima™ resin also seems to have a low glass transition temperature of only 124 °C [16]. The typical T_g value for pure DCPD as transformed by a RIM process is 155°C (by DSC) and the T_g of the F2.06 PDCPD formulation used in the present study is even 215°C.

In the study, the researchers reported similar in-plane mechanical properties compared to an epoxy counterpart, and found a very high G_{Ic} value for the PDCPD composite of 1729 J/m². The tensile fatigue performance observed in [13-15] was similar to that of the epoxy composites, while a slightly improved compressive fatigue resistance was observed for the PDCPD laminates. Tests on a complex structured coupon with two ply drops revealed an increase of about 30 % in the static load required for large-scale delamination in the PDCPD composite, as well as higher reversed loading fatigue cycles to obtain the same damage length in the complex coupon [15].

The present paper contains the results of an exploratory study, analysing several aspects of the mechanical performance and damage behaviour of glass fibre reinforced composites with a special high T_g PDCPD grade (T_g = 215°C) for the matrix, as compared to an equivalent (brittle) epoxy composite. The mode I interlaminar fracture toughness, the quasi-static and fatigue tensile behaviour, the compression strength, the impact behaviour and the compression after impact strength were studied.

2 MATERIALS AND EXPERIMENTS

2.1 Materials

The matrix materials used for this study were a specialty DCPD based formulation (type F2.06) with high T_g, and a standard epoxy resin (Epikote 828 LVEL with Dytek DCH 99 hardener [17]), see table 1.

Two types of E-glass fibres were used: For the epoxy composites, PPG 1383 was used. Since typical glass sizing formulations used in commercial glass fibres are compatible with polar epoxy matrices and incompatible with the non-polar F2.06 formulation a special type of fibre, T73, with a DCPD-compatible sizing, was used for the PDCPD. Both types of glass were available as rovings (direct draw) and as a plain woven fabric with an areal density of 800 g/m².

Unidirectional laminates with a centred crack starting foil for the interlaminar toughness tests were produced by dry winding and then vacuum infusion. Woven fabric laminates were produced by vacuum infusion of 4 plain weave fabric layers.

	PDCPD F2.06	Epikote 828 LVEL + DCH-99
Density (kg/dm³)	1.03	1.16
Modulus (GPa)	1.9	3 [18]
Initial viscosity @25°C (Pas)	< 0.01	10-12 [17]
Tensile Strength (MPa)	60	75 [18]
Elongation at break (%)	*At yield: 5*	4 [18]
Glass transition temp. (°C) (DMA)	215	155

Table 1: Physical, thermal and mechanical properties for the matrices studied in this work.

2.2 Experiments

Interlaminar fracture toughness mode I tests (double cantilever beam tests) were done on unidirectional samples with a centred crack starter film. The tests were done in accordance with the ISO 15024 standard. As specified in the standard, a preloading procedure was used to generate a precrack for the tests.

Samples cut from the woven fabric laminates were subjected to quasi-static tensile tests with a crosshead speed of 2 mm/min, following ASTM 3039. Strain was measured either by means of digital image correlation (DIC) over a region of 25x25 mm² or by means of an extensometer with a gauge length of 50 mm.

A series of fatigue tests was run on both types of materials with a frequency of 5 Hz and an R-ratio of 0.1. ASTM 3479 was followed. Tests were done at approximately 50, 40, and 30% of the tensile strength.

Compression tests were done with a test speed of 1.5 mm/min. Strain was measured on both sides of the samples by means of DIC, to ensure there was no excessive bending present, in accordance with the procedure of ISO 14126.

Samples of 150x100x4 mm³ were impacted with an energy of approximately 7J per mm thickness (and for the PDCPD also 12.4 J/mm) and then tested in compression to determine the compression strength after impact (CAI). The size of the impact damage was assessed by means of ultrasonic C-scan. During the CAI tests, the percentage of bending was again monitored by means of DIC on both sides of the samples.

3 RESULTS AND DISCUSSION

3.1 Interlaminar fracture toughness

The R-curves for the mode I interlaminar toughness are in Figure 1. Both the initiation values from the insert (crack length from insert = 0) and from the precrack (second set of points) are shown. In both cases, $G_{Ic\ init}$ is about three times higher for the PDCPD composite than for the epoxy composite. The value from the precrack for the PDCPD composite is 1065 J/m², which is in the range commonly observed for composites with highly-toughened epoxies [19-22] and even some PEEK [23, 24]. In [13-15], a much higher value was found for a glass-PDCPD composite, but the PDCPD in that case was a very different formulation. Also for the propagation stage, the G_{Ic} values are much higher (about two times) for the PDCPD composite than for the epoxy composite. These results indicate that PDCPD composites indeed have very good resistance to initiation and growth of delaminations.

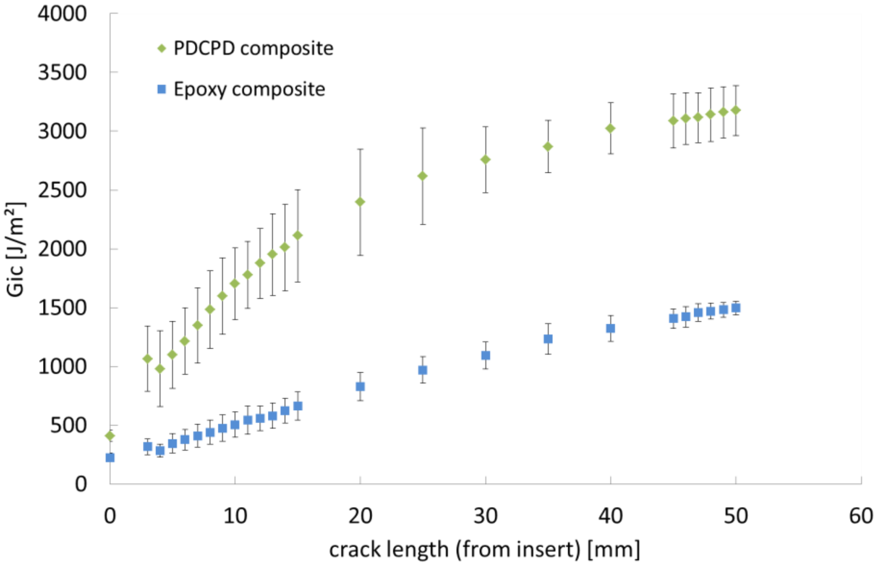

Figure 1: R-curves for the two composite materials with initiation and propagation toughness values. Initiation values are determined by the 5% offset method.

3.2 Tensile behaviour

Quasi-static

No significant difference between the two materials was measured in terms of stiffness, even after normalising the results to the same fibre volume fraction (50 %). The strength as-measured also showed no difference, but after normalisation, the strength of the PDCPD laminate was found to be about 9 % higher than that of the epoxy composite.

The biggest difference was seen in the development of damage during the test (see figure 2). In the epoxy laminate the classical behavior for thermoset matrix composites was observed: first, a rapid initiation and growth of transverse matrix cracks, later followed by longitudinal cracks and metadelaminations on the cross-over points in the weaves, and finally large-scale delamination leading to failure. In the PDCPD composite, however, initiation of transverse cracks was greatly delayed and the observed cracks were much shorter and less numerous. Also the formation of meta- and large scale delaminations was almost completely suppressed in this material. Final failure was very localized. This high resistance to damage initiation and delamination is consistent with the observed high G_{Ic}.

Fatigue

The fatigue life data and the 95% confidence region for the data are shown in figure 3. It is clear that the fatigue life data for the PDCPD composite are situated in the higher range of the epoxy composite data and that the variation on the fatigue life is much smaller for the former. Damage development during fatigue was also monitored for some samples and similar trends as in the quasi-static tests were observed: transverse cracks form later and are much less numerous in the PDCPD composite than in the epoxy composite. The formation of delaminations is much less and failure is very localized, where in the epoxy composite, delaminations start to form early in the fatigue life and failure is associated with large-scale delamination and dispersed fibre failure.

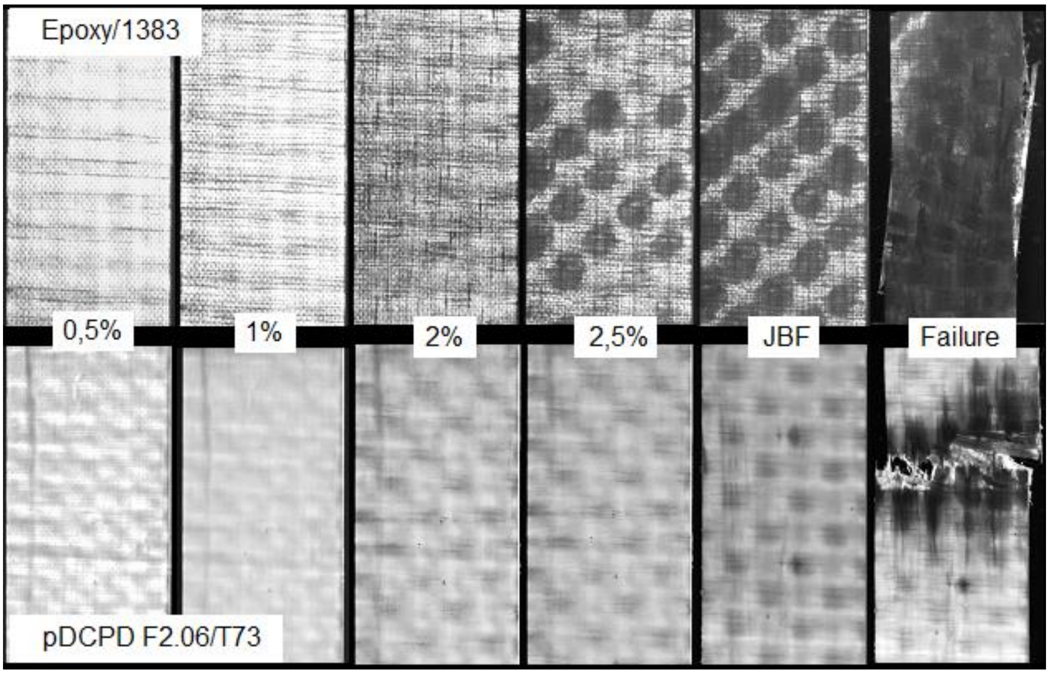

Figure 2: transmitted light pictures of the damage development during a static test.

As a result of the difference in damage development, differences in modulus evolution were also noted. The decrease in modulus for the epoxy composite was more than twice that for the PDCPD composite.

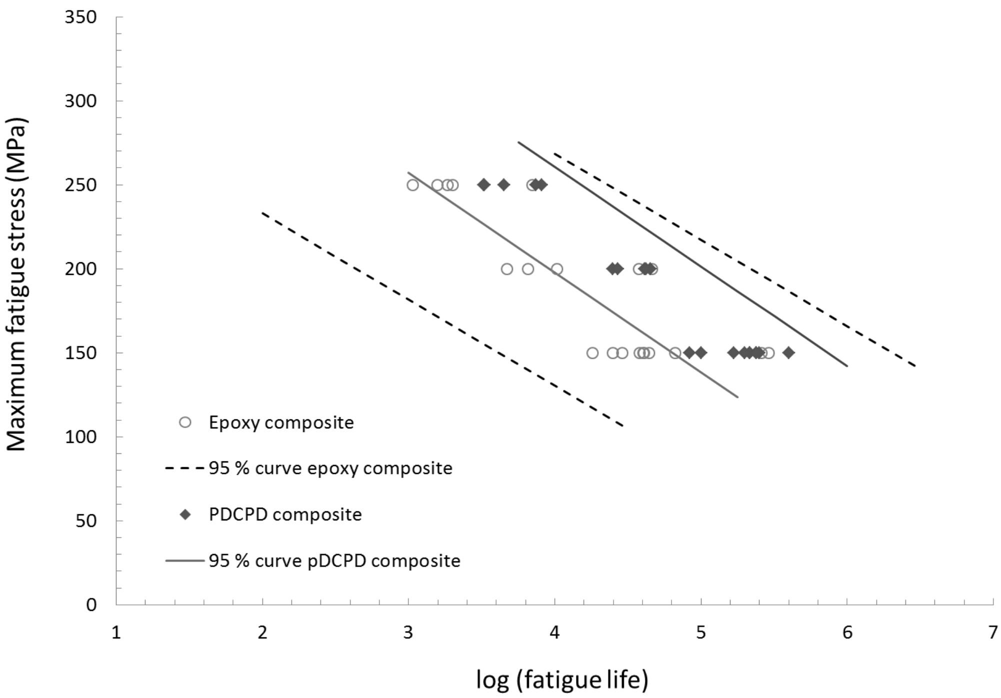

Figure 3: Fatigue life data for the two materials. The 95-95 fatigue life region is also shown.

3.3 Compression behavior

	PDCPD composite	Epoxy composite
Compressive modulus [GPa]	21,4 ± 0,2	22,9 ± 0,7
Compressive strength [MPa]	289 ± 13	246 ± 25
Normalised modulus [GPa]	20,2 ± 0,2	22,9 ± 0,7
Normalised strength [MPa]	273 ± 12	246± 25

Table 2: Results of the compression tests as-measured and normalized to the same Vf.

The compression strength and stiffness for the woven fabric laminates are listed in table 2. No excessive bending or buckling were observed during the tests. A higher compressive strength but a lower modulus were observed for the PDCPD laminate. These observations can be explained by the lower modulus of PDCPD compared to epoxy (1.9 vs. 3 GPa), and the higher resistance to delamination and crack formation (higher toughness).

3.4 Impact and compression after impact behavior

Visual inspection of the impact damage indicated that the damaged area in the epoxy laminate was much larger than that in the PDCPD laminate for the same impact energy and thickness of the samples. Also, the epoxy composite showed a region with many matrix cracks around the impact site, which was not seen in the PDCPD composite (see figure 4). The results of the ultrasonic c-scan are shown in figure 5. They confirm the visual observations: for an impact energy of 7J/mm, the projected area of delamination is about twice as large in the epoxy composite as in the PDCPD. The projected area of delamination for the epoxy laminate after 7J/mm was even larger than that for the PDCPD laminate after 12.4 J/mm. Again, these results are very consistent with the observations above, and can be explained by the tougher nature of the PDCPD matrix.

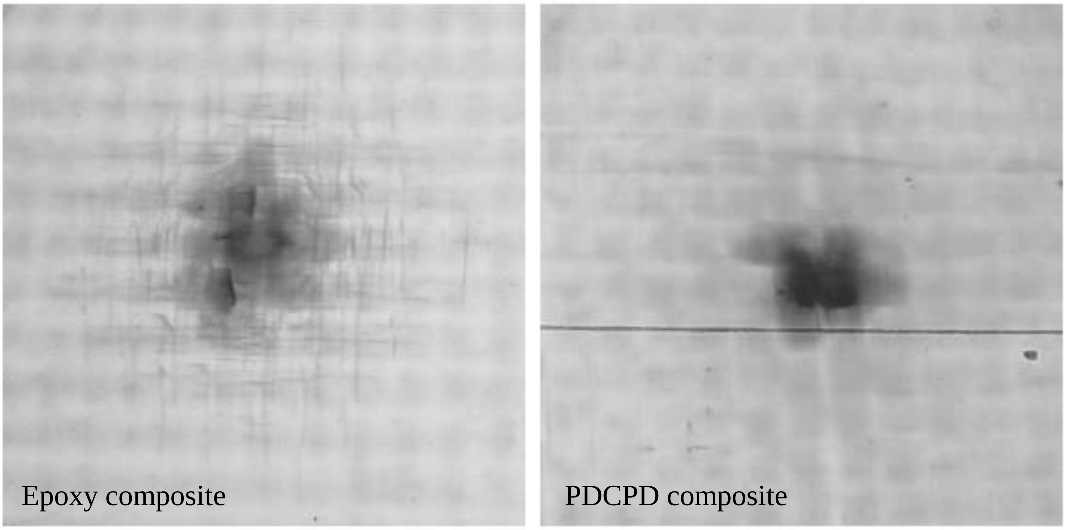

Figure 4: transmitted light pictures of impact damage in the two types of laminates.

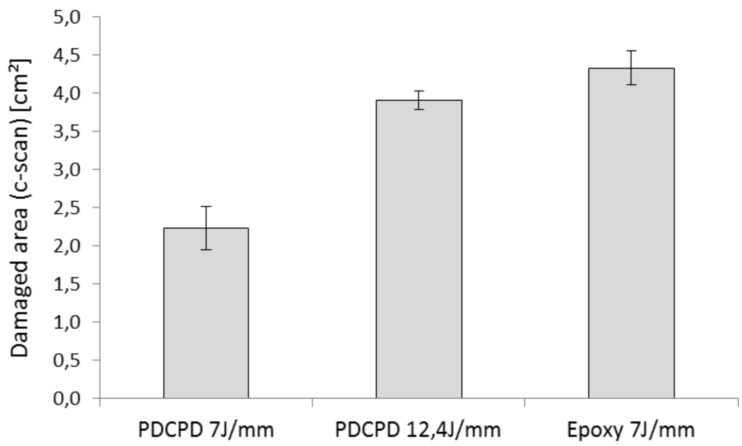

Figure 5: Impact damage area measured by C-scan

The compression after impact strength for the different types of samples is shown on the graph in figure 6. The more limited impact damage, combined with the higher resistance to delamination growth in the PDCPD laminate is clearly reflected in a higher compression after impact strength. The CAI strength of the PDCPD laminate after 7J/mm is about 20% higher than that of the epoxy laminate after 7 J/mm. Even after the higher impact energy of 12.4 J/mm, the strength is still 10 % higher than that of the epoxy composite.

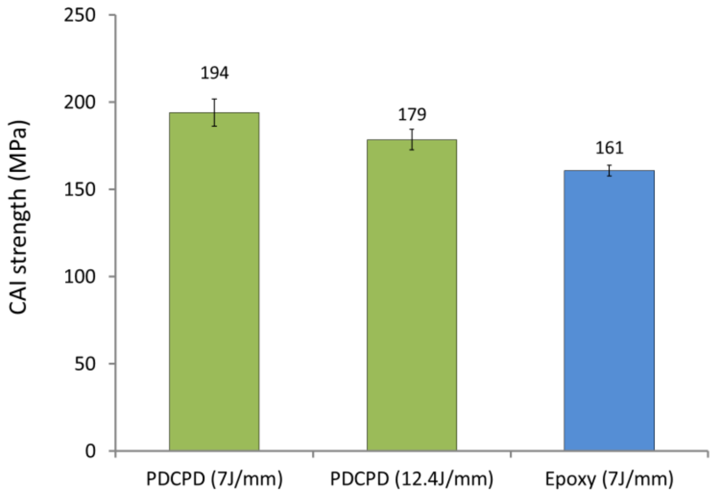

Figure 6: compression after impact strength results

4 SUMMARY

A range of properties were assessed for composites with a PDCPD formulation matrix, and benchmarked against those of an equivalent standard brittle epoxy composite. Higher interlaminar fracture toughness was measured for the PDCPD composite, which was consistent with the much reduced damage development as observed in the static and dynamic tensile test and the impact tests. The fatigue life for the PDCPD composite was found to be higher, as well as the compression strength. The reduction in impact damage and the higher interlaminar toughness lead to a higher compression after impact strength. The findings clearly demonstrate that this type of PDCPD has high potential as a matrix for damage tolerant, tough thermoset composites.

5 REFERENCES

1. Bagheri, R., B.T. Marouf, and R.A. Pearson, *Rubber-Toughened Epoxies: A Critical Review*. Polymer Reviews, **49**(3): p. 201-225, 2009.
2. Ratna, D. and A. Banthia, *Rubber toughened epoxy*. Macromolecular Research, **12**(1): p. 11-21, 2004.
3. Bull, D.J., S.M. Spearing, and I. Sinclair, *Investigation of the response to low velocity impact and quasi-static indentation loading of particle-toughened carbon-fibre composite materials*. Composites Part A: Applied Science and Manufacturing, **in press**, 2015.
4. Fenner, J.S. and I.M. Daniel, *Hybrid nanoreinforced carbon/epoxy composites for enhanced damage tolerance and fatigue life*. Composites Part A: Applied Science and Manufacturing, **65**(0): p. 47-56, 2014.
5. Poon, C., T. Benak, and R. Gould, *Assessment of impact damage in toughened resin composites*. Theoretical and Applied Fracture Mechanics, **13**(2): p. 81-97, 1990.
6. Vieille, B., V.M. Casado, and C. Bouvet, *Influence of matrix toughness and ductility on the compression-after-impact behavior of woven-ply thermoplastic- and thermosetting-composites: A comparative study*. Composite structures, **110**(0): p. 207-218, 2014.
7. Vieille, B., V.M. Casado, and C. Bouvet, *About the impact behavior of woven-ply carbon fiber-reinforced thermoplastic- and thermosetting-composites: A comparative study*. Composite structures, **101**(0): p. 9-21, 2013.
8. Bishop, S.M., *The mechanical performance and impact behaviour of carbon-fibre reinforced PEEK*. Composite structures, **3**(3–4): p. 295-318, 1985.
9. Manjunatha, C.M., A.C. Taylor, A.J. Kinloch, and S. Sprenger, *The tensile fatigue behaviour of a silica nanoparticle-modified glass fibre reinforced epoxy composite*. Composites Science and Technology, **70**(1): p. 193-199, 2010.
10. Manjunatha, C.M., S. Sprenger, A.C. Taylor, and A.J. Kinloch, *The Tensile Fatigue Behavior of a Glass-fiber Reinforced Plastic Composite Using a Hybrid-toughened Epoxy Matrix*. journal of composite materials, **44**(17): p. 2095-2109, 2010.
11. Böger, L., J. Sumfleth, H. Hedemann, and K. Schulte, *Improvement of fatigue life by incorporation of nanoparticles in glass fibre reinforced epoxy*. Composites Part A: Applied Science and Manufacturing, **41**(10): p. 1419-1424, 2010.
12. Drozdzak, R., G. Recher, and A. Daemen, *pDCPD: a specialty thermoset with a bright future*, in *Thermosets 2009*, Berlin, Germany. p. 42-45, 2009.
13. Mandell, J.F., D.D. Samborsky, P. Agastra, A.T. Sears, T.J. Wilson, T. Ashwill, and D. Laird, *Analysis of SNL/MSU/DOE Fatigue Database Trends for Wind Turbine Blade Materials* Contractor Report SAND2010-7052, Sandia National Laboratories, Albuquerque, NM. p. 163-169, 2010.
14. Samborsky, D.D., P. Agastra, and J.F. Mandell, *Fatigue trends for wind blade infusion resins and fabrics*, in *AIAA SDM, Wind energy session*, Orlando, 2010.
15. Agastra, P. and J.F. Mandell, *Testing and simulation of damage growth at ply drops in wind turbine blade laminates*, in *Proceedings of society of the advancement of materials and process engineering (SAMPE)*, Seattle, WA, 2010.
16. Hu, Y., A.W. Lang, X. Li, and S.R. Nutt, *Hygrothermal aging effects on fatigue of glass fiber/polydicyclopentadiene composites*. Polymer Degradation and Stability, **110**(0): p. 464-472, 2014.
17. *Epikote 828 LVEL - TDS*. Available from: http://www.team-well.com/upload/1170838779617.pdf.
18. Callens, M., *Development of ductile stainless steel fibre composites*, PhD dissertation, Department of Materials Engineering, KULeuven, 2014.
19. Romhány, G. and G. Szebényi, *Interlaminar crack propagation in MWCNT/fiber reinforced hybrid composites*. eXPRESS Polymer Letters, **3**: p. 145-151, 2009.
20. Davallo, M., *Factors Affecting Fracture Behaviour of Composite Materials*. International Journal of ChemTech Research, **2**(4): p. 2125-2130, 2010.

21. Zhang, J., S. Deng, L. Ye, and Z. Zhang. *Interlaminar Fracture Toughness and Fatigue Delamination Growth of CF/EP Composites with Matrices Modified by Nano-silica and CTBN rubber*. in *13th International Conference on Fracture*, Beijing, China. 2013.
22. Tsai, J.L., B.H. Huang, and Y.L. Cheng, *Enhancing Fracture Toughness of Glass/Epoxy Composites for Wind Blades Using Silica Nanoparticles and Rubber Particles.* Procedia Engineering, **14**(0): p. 1982-1987, 2011.
23. Davies, P., H.H. Kausch, J.G. Williams, A.J. Kinloch, M.N. Charalambides, A. Pavan, D.R. Moore, R. Prediger, I. Robinson, N. Burgoyne, K. Friedrich, H. Wittich, C.A. Rebelo, A. Torres Marques, F. Ramsteiner, B. Melve, M. Fischer, N. Roux, D. Martin, P. Czarnocki, D. Neville, I. Verpoest, B. Goffaux, R. Lee, K. Walls, N. Trigwell, I.K. Partridge, J. Jaussaud, S. Andersen, Y. Giraud, G. Hale, and G. McGrath, *Round-robin interlaminar fracture testing of carbon-fibre-reinforced epoxy and PEEK composites.* Composites Science and Technology, **43**(2): p. 129-136, 1992.
24. Sela, N. and O. Ishai, *Interlaminar fracture toughness and toughening of laminated composite materials: a review*. Composites, **20**(5): p. 423-435, 1989.